A PHENOMENOLOGICAL MODEL
OF THERMOPHOTOTROPISM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

An equation is developed which describes the phenomenology of thermophototropism. The equation could have application to thermal analysis and, hence, be used in a feasibility study on thermophototropes for temperature control in the space environment. A literature survey is included in the appendix.

CONTENTS

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INTRODUCTION

Thermophototropism, or temperature-dependent variable absorptivity, is the explicit designation of a phenomenon known variously as phototropism, thermotropism, or both. The term "thermophototropism," although a bit unwieldy, cannot be misinterpreted as can one of the latter, "phototropism," which has a biological connotation. The importance of formulating a phenomenological model of thermophototropic materials was twofold. First, it would give a physical basis on which various experimental observations could be correlated and, second, it would be of use in thermal design.

The materials have been found as members of both major classes of chemical compounds, inorganic and organic. Inorganic thermophototropes can be classified with respect to their anion constituent, oxygen or sulfur. With oxygen present, the martrix and doping cations are members of group II, III, V, or VI in the periodic table; whereas, with sulfur present, the cation is mercury (IIa). The oxide compounds (most of which are reversible) derive their behavior from:

1. Surface oxidation in the presence of oxygen, moisture, or both;

2. Internal impurity adsorption on the surfaces of the individual microcrystalline hosts;

3. Vacancy migration;

4. Internal oxidation.

The mercuric compounds (most of which are irreversible) derive their behavior from:

1. Phase changes;

2. Diffusion mechanisms;

3. Oxidation and reduction reactions (in the presence of light, oxygen, or both).

Because reversibility is necessary for thermal coating applications, this phenomenonological development of a model of thermophototropism is applicable only to reversible materials. The next section, which is concerned with the phenomenology of thermophototropism, is developed from

1

certain qualitative experimental observations on these materials.* In the succeeding section, a partial differential equation (to which a solution is found) is developed from the phenomenology. The final section is devoted to a discussion of the equation and to the possible application of optical measurements in the evaluation of certain parameters in the solution. The inorganic materials mentioned in the body of the report as well as additional ones are discussed in Appendix A. Also, organic substances are briefly considered.

PHENOMENOLOGY OF THERMOPHOTOTROPISM

Since a phenomenological model of the temperature-dependent variable absorptivity property possessed by certain materials must be capable of reproducing certain gross experimental observations,* it is the purpose of this section to present and elucidate these observations, in preparation for the mathematical development of the model.

As the name "thermophototropism" implies, the energy absorbed by a thermophototrope is dependent upon its photoresponse, i.e., its change in absorptivity with time at a particular temperature and illumination level. For example, should a given sample happen to be in its minimum absorptivity state at a given temperature, upon illumination we would expect its absorptivity in the visible range of the spectrum to increase to a maximum value governed by the temperature of the sample. Likewise, with the removal of illumination, the absorptivity would gradually return to its minimum value, the rate of return being dependent upon temperature.

The thermal dependence of the absorptivity of these materials may be divided into four regions. In two of these regions thermophototropes cannot respond temporally; i.e., if a sample is at either too low or too high a temperature its absorptivity cannot be changed from its minmum value by solar radiation. Consequently, whenever the temperature is less than some critical level T_0, absorptivity changes are, at best, imperceptively slow. Further, by adiabatically reducing a darkened sample to T_0, its absorptivity can be frozen in. Likewise, whenever the temperature is equal to or greater than a certain level, T_u, darkening becomes impossible. Therefore, as the temperature is raised from the minimum critical value T_0 a third temperature region is encountered, in which positive increments in temperature exert a synergistic effect with photon flux in producing an enhancement in the darkening ability of a given sample; i.e., $\partial \alpha/\partial T$ must be positive, where α and T represent absorptivity and temperature, respectively. Consequently, a temperature T_c, lying between T_0 and T_u, will be reached at which $\partial \alpha/\partial T$ is zero. The fourth temperature region is that in which further increments in temperature result in a negative value for $\partial \alpha/\partial T$. This division into four regions also applies to any sublayer of a sample.

Finally, the overall behavior of a material will necessarily be dependent upon the illumination intensity and spectral distribution. It is clear then that the energy absorbed, W, and α can be represented in the functional form:

$$W = W(\alpha) \; ,$$

where

$$\alpha = \alpha\Big\{t\big[I(\lambda)\big], \; x\big[I(\lambda)\big], \; T\big[I(\lambda)\big]\Big\},$$

with

   t = time exposed to illumination,

   x = depth measured from the surface (a positive value),

   T = temperature,

$I(\lambda)$ = spectral intensity.

The effects of illumination intensity and spectral distribution can be assessed only from optical measurements and microscopic theory. Consequently, the $I(\lambda)$ dependence will be implicitly understood in the next section in connection with the determination of proportionality and integration constants. Therefore $\alpha = \alpha[t,x,T; \; I(\lambda)]$.

MATHEMATICAL DEVELOPMENT

Now a partial differential equation will be derived which, when solved, can be used in describing, qualitatively, the temporal, thermal, and depth dependences of the materials. Since the change in the energy absorbed relative to the absorptivity minimum is time-dependent,

$$\frac{\partial W}{\partial\,(t\,-\,t_M)}\bigg|_{x,T}$$

is the required first order contribution at an arbitrary depth x and temperature T. The derivative is written in terms of a relative time because the response depends upon how much time has passed since the material was in its maximum absorptivity state located in time at t_M. This derivative has a positive sign because ΔW and $t - t_M$ are both negative. Similarly, the inclusion of temperature to the first order gives the expression

$$-\tau\,\frac{\partial W}{\partial(T\,-\,T_c)}\bigg|_{t,x} \quad ,$$

where again the independent variable has been written in relative form since the temperature gradient of the absorptivity may be positive or negative, depending on whether T is greater or less than T_c. A thermal response τ must be included because darkening is dependent upon the response of the material to any temperature change which occurs as a result of illumination.

The energy penetration term is

$$u \left. \frac{\partial W}{\partial(x - x_o)} \right|_{t,T} + u\eta W \left. \right|_{t,T} ,$$

where u and η are the penetration velocity and absorption index, respectively; the derivative is taken relative to an arbitrary reference point x_0 in order to identify penetration from any chosen layer. This relation is clearly the case because the gradient across any infinitesimal layer is dependent not only upon the rate at which the darkened layer progresses into the material from a chosen layer, but also upon the rate of energy absorption in that layer. Finally, the total change in the relative energy absorbed is

$$\frac{dW}{dt} = \frac{\partial W}{\partial(t - t_M)} - \frac{\partial W}{\partial(T - T_c)} \tau + u \frac{\partial W}{\partial(x - x_0)} + u\eta W . \tag{1}$$

Before writing Equation 1 in terms of absorptivity, two regions for the spectral distribution must be defined. The first region contains wavelengths up to a critical magnitude; the second region contains the remainder. It has been experimentally observed that wavelengths greater than the critical one may cause bleaching (a decrease in absorptivity), whereas those which are shorter induce darkening.* Therefore,

$$W = A_p I \int_0^t (\alpha - \alpha_0) \, d\zeta , \tag{2}$$

where

A_p = projection of sample area normal to the incident illumination,

I = illumination intensity,

α = absorptivity at wavelengths less than the critical value,

α_0 = minimum absorptivity,

and W is (as mentioned in the previous section) the incremental energy absorbed relative to that absorbed at α_0. Substituting Equation 2 into Equation 1 yields

$$\frac{d(\alpha - \alpha_0)}{dt} = \frac{\partial(\alpha - \alpha_0)}{\partial(t - t_M)} - \frac{\partial(\alpha - \alpha_0)}{\partial(T - T_c)} \tau + u \frac{\partial(\alpha - \alpha_0)}{\partial(x - x_0)} + u\eta(\alpha - \alpha_0) , \tag{3}$$

since the integral must be uniformly convergent. Expressing $d(\alpha - \alpha_0)/dt$ as $(\alpha - \alpha_0)/t$ and rewriting Equation 3 gives

$$\frac{\partial(\alpha - \alpha_0)}{\partial(t - t_M)} - \frac{\partial(\alpha - \alpha_0)}{\partial(T - T_c)} \tau + u \frac{\partial(\alpha - \alpha_0)}{\partial(x - x_0)} + u\eta(\alpha - \alpha_0) - \frac{\alpha - \alpha_0}{t} = 0 , \tag{4}$$

where the state α is now set at $t = 0$.

We can make the substitution

$$\alpha - \alpha_0 = g(t)\, f(T)\, h(x) \,, \tag{5}$$

to obtain the solution:

$$\alpha = \alpha_0 + (\text{const.})\, t \, \exp - \left[S_1\left(t - t_M\right) + \frac{S_2}{\tau}\left(T - T_c\right) + \frac{S_2 - S_1 + u\eta}{u}\left(x - x_0\right) \right]. \tag{6}$$

There remains the problem of obtaining the integration constant and S_1 and S_2, the separation constants. The integration constant may be found by observing that the maximum absorptivity, α_M, for a given illumination intensity and spectral distribution is defined when $t = t_M$, $T = T_c$, and $x = x_0$, from which it follows that

$$\alpha_M = \alpha_0 + (\text{const.})\, t_M$$

or

$$\text{const.} = \frac{\alpha_M - \alpha_0}{t_M} \,,$$

and

$$\alpha = \alpha_0 + \left(\alpha_M - \alpha_0\right) \frac{t}{t_M} \, \exp - \left[S_1\left(t - t_M\right) + \frac{S_2}{\tau}\left(T - T_c\right) + \frac{S_2 - S_1 + u\eta}{u}\left(x - x_0\right) \right] \tag{7}$$

The first separation constant S_1 may be determined by partially differentiating Equation 7 with respect to t :

$$\frac{\partial \alpha}{\partial t} = \left(\alpha_M - \alpha_0\right)\left(1 - tS_1\right)\frac{1}{t_M} \, \exp - \left[S_1\left(t - t_M\right) + \frac{S_2}{\tau}\left(T - T_c\right) + \frac{S_2 - S_1 + u\eta}{u}\left(x - x_0\right) \right]$$

and since

$$\left.\frac{\partial \alpha}{\partial t}\right|_{t = t_M,\ x = x_0,\ T = T_c} = 0 \,,$$

then

$$S_1 = \frac{1}{t_M} \,.$$

5

Since Equation 4 is a first order partial differential equation, it amounts to a specified geometric relation between slopes parallel to the various three-dimensional hyperplanes in the four space defined by α, t, τ, and x. An immediate consequence of this relationship is the following system of ordinary differential equations:

$$d\left(t - t_M\right) = -\frac{d\left(T - T_c\right)}{\tau} = \frac{d\left(x - x_0\right)}{u} = \frac{d\left(\alpha - \alpha_0\right)}{\left(-u\eta + \frac{1}{t}\right)\left(\alpha - \alpha_0\right)} \,,\tag{8}$$

where the number of independent variables has been increased by one by means of the transformation:

$$Z = Z\left[y_i, \left(\alpha - \alpha_0\right)\right] \,.\tag{9}$$

By virtue of

$$\frac{\partial Z}{\partial y_i} + \frac{\partial Z}{\partial\left(\alpha - \alpha_0\right)}\ \frac{\partial\left(\alpha - \alpha_0\right)}{\partial y_i} = 0 \,,\tag{10}$$

Equation 4 can now be written:

$$\frac{\partial Z}{\partial\left(t - t_M\right)} - \frac{\partial Z}{\partial\left(T - T_c\right)}\ \tau + u\ \frac{\partial Z}{\partial\left(x - x_0\right)} - u\eta\left(\alpha - \alpha_0\right)\frac{\partial Z}{\partial\alpha} + \frac{\alpha - \alpha_0}{t}\frac{\partial Z}{\partial\alpha} = 0 \,.\tag{11}$$

Equation 8 is an immediate consequence of Equation 11. Integration of the first part of Equation 8 gives

$$t - t_0 = -\frac{1}{\tau}\left(T - T_0\right).\tag{12}$$

Because letting $t = t_M$ is equivalent to setting $T = T_c$, it is clear from Equations 7 and 8 that multiplying both sides of Equation 12 by S_1 will show S_2 equal to S_1,

$$S_1 = S_2 = \frac{1}{t_M} \,.$$

Equation 11 also serves to relate t_M and T_c,

$$t_M = -\frac{1}{\tau}\left(T_0 - T_c\right) \,,$$

by virtue of Equation 8 where t or any reference time t_0 is equal to 0. T_0 has now been identified as the first critical temperature, described in the previous section.

Likewise, from the integration of

$$dt = \frac{d\left(x - x_0\right)}{u} ,$$

u, the velocity at which the lowest measurable darkening level progresses through the material, may be evaluated:

$$t_L = \frac{L}{u}$$

or

$$u = \frac{L}{t_L} ,$$

where L is the sample thickness and t_L is the time required for measurable darkening to take place on the unilluminated surface.

In order to evaluate τ, the thermal response, assume that the sample is at uniform temperature apart from heating due to radiation absorption. Consequently, at the surface

$$mC_p\tau \approx \gamma I\alpha_0\left(1 - \beta_v\right) + I\alpha_0\left(1 - \gamma\right) - \epsilon\,\sigma\,T^4$$

or

$$\tau \approx \frac{\gamma I\alpha_0\left(1 - \beta_v\right)}{mC_p} + \frac{I\alpha_0\left(1 - \gamma\right)}{mC_p} - \frac{\epsilon\,\sigma\,T^4}{mC_p} , \qquad (13)$$

where

   m = mass of the sample,

   C_p = heat capacity at constant pressure,

   γ = fraction of illumination responsible for phototropic change in the sample,

   β_v = quantum efficiency of the wavelength band in the neighborhood of the critical wavelength,

   ϵ = sample emittance,

   σ = Stefan-Boltzmann constant.

(14)

The final result is:

$$\alpha = \alpha_0 + \left(\alpha_M - \alpha_0\right) \frac{t}{t_M} \exp - \left[\frac{t - t_M}{t_M} + \frac{T - T_c}{\tau t_M} + \eta\left(x - x_0\right)\right] . \tag{15}$$

After being illuminated to a given level of absorptivity where

$$\alpha_0 \leq \alpha \leq \alpha_M ,$$

a thermophototrope will bleach from α to α_0. Consequently, in the absence of illumination,

$$\frac{dW}{dt} = 0 ;$$

and Equation 4 becomes:

$$\frac{\partial\left(\alpha - \alpha_0\right)}{\partial\left(t - t_\xi\right)} - \frac{\partial\left(\alpha - \alpha_0\right)}{\partial\left(T - T_c\right)} + u \frac{\partial\left(\alpha - \alpha_0\right)}{\partial\left(x - x_0\right)} + u\eta\left(\alpha - \alpha_0\right) = 0 , \tag{16}$$

where t_ξ is the exposure time. From Equation 16

$$\alpha = \alpha_0 + \left(\alpha_M - \alpha_0\right) \exp - \left[\delta_1 \left(t - t_\xi\right) + \frac{\delta_1}{\tau}\left(T - T_c\right) + \eta \left(x - x_0\right)\right] \tag{17}$$

If δ_1 is defined as the relative time required for the absorptivity to decay to the eth part at a given T and x, then

$$\delta_1 = \frac{1}{t_0 - t_\xi} , \tag{18}$$

which gives

$$\alpha = \alpha_0 + (\text{const.}) \exp - \left[\frac{t - t_\xi}{t_0 - t_\xi} + \frac{T - T_c}{\tau_\xi\left(t_0 - t_\xi\right)} + \eta_\xi\left(x - x_0\right)\right] , \tag{19}$$

where $t \geq t_\xi$; τ_ξ and η_ξ identify the decay of their respective parts of the exponential at a given temperature and depth and consequently are defined by the eth part of their contributions:

$$\tau_\xi = \frac{T_\xi - T_c}{t_0 - t_\xi} , \tag{20}$$

and

$$\eta_\xi = \frac{1}{x_\xi - x_0} . \tag{21}$$

At time t_ξ, temperature T_ξ, and depth x_ξ

$$\left(\alpha_\xi - \alpha_0\right)_{t_\xi,\ darkening} = \left(\alpha_\xi - \alpha_0\right)_{t_\xi,\ bleaching} \ . \tag{22}$$

From Equations 15 and 22 the constant in Equation 19 may be found:

$$const. = \left(\alpha_M - \alpha_0\right)\frac{t_\xi}{t_M} \exp - \left[\frac{t_\xi - t_M}{t_M} + \frac{T_\xi - T_c}{\tau t_M} - \frac{T_\xi - T_c}{\tau_\xi\left(t_0 - t_\xi\right)} + \eta\left(x_\xi - x_0\right) - \eta_\xi\left(x_\xi - x_0\right)\right] \ . \tag{23}$$

The resultant decay is therefore, by virtue of Equations 19 and 23:

$$\alpha = \alpha_0 + \left(\alpha_M - \alpha_0\right)\left\{\frac{t_\xi}{t_M} \exp - \left[\frac{t_\xi - t_M}{t_M} + \frac{T_\xi - T_c}{\tau t_M} - \frac{T_\xi - T_c}{\tau_\xi\left(t_0 - t_\xi\right)} + \eta\left(x_\xi - x_0\right) - \eta_\xi\left(x_\xi - x_0\right)\right]\right\} \ .$$

$$\cdot \ \exp - \left[\frac{t - t_\xi}{t_0 - t_\xi} + \frac{T - T_c}{\tau_\xi\left(t_0 - t_\xi\right)} + \eta_\xi\left(x - x_0\right)\right] \ . \tag{24}$$

In order to set a bound on the temperature T_u (the maximum temperature, at which α_0 is the only possible absorptivity state) let $x_\xi = x_0$, $t = t_M$, and $T = T_u$ in Equation 15:

$$T_u = n\tau t_M + T_c \ , \tag{25}$$

where n is the eth part to be taken. Again T_u has been defined in a manner similar to t_0 ; i.e., decay to the eth part.

DISCUSSION

It is clear that Equation 15 qualitatively fits the phenomenology of thermophototropism presented in the first section. A reasonable temporal variation of absorptivity has been found and the synergy of time and temperature reproduced. Derivation relative to the parameters α_0 , t_M, and T_c , the magnitudes of which can be found by experimentation, facilitated the formulation of the first order differential. Had this not been done, it would have been necessary to extend the derivation in a manner analogous to derivations of the Navier-Stokes equations. Such an extension would have led to equations which are not amenable to solution. This fact justifies the approach, because an equation has been developed which, after "calibration," can reproduce the thermophototropic property.

Evaluation of the parameters α_0 , α_M, t_M, T_c , T_0 , τ, and η is a matter of experimentation. The α's may be found spectrophotometrically, once the effect of beam intensity on a given material has been determined. The values of t_M and T_c must be found simultaneously, by trial, and may be checked for consistency with Equation 8. T_0 and T_u may be found simply from simultaneous illumination and heating experiments. The value for τ can be found from Equations 13, once β_v is found from optical
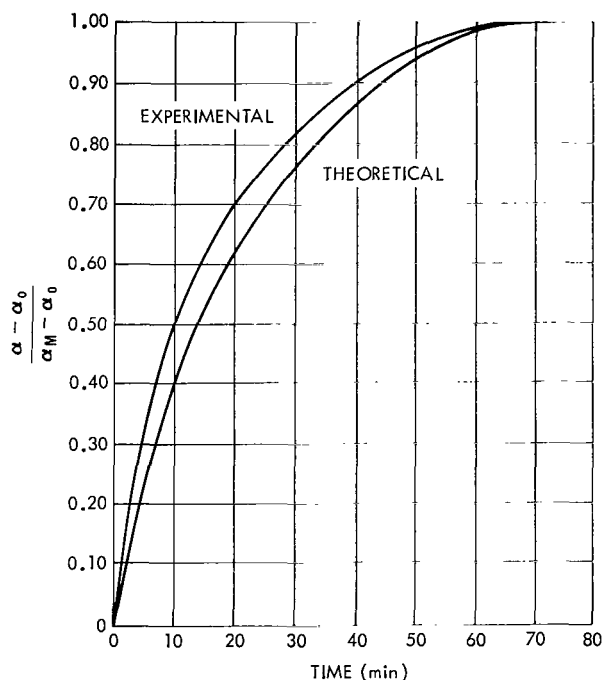
Figure 1—A comparison of theoretical and experimental incremental absorptivity curves for barium titanate at 550 mμ.

measurements. And η is defined once β_v is known and $\bar{\eta}$ has been evaluated by means of optical transmission measurements. T_u and t_0 are defined from their respective eth parts, since Equation 15 give no upper bounds for T and t.

In an effort to demonstrate the potential usefulness of Equation 15, comparison plots of Equation 15 and data from NASA contract NAS 5-582* are given in Figure 1, where relative incremental absorptivity is the ordinate and time the abscissa. The agreement is quite good; however, it must be remembered that the data for the experimental curve were not taken expressly for theoretical evaluation, but rather to give qualitative trends. It is certain that, when the samples were exposed, conditions were not isothermal; consequently, since T_c was probably above room temperature, the synergistic effect mentioned earlier probably was present.

*NASA contract NAS 5-582, Seventh Quarterly Progress Report, Lexington Laboratories, Cambridge, Massachusetts, p. 14a.

Appendix A

Literature Survey on Phototropism

Takei (References A1-A4) has studied, extensively, mercuric compounds of the forms $HgX_2 \cdot 2HgS$ and $HgXCNS \cdot 2HgS$ (where X is a halogen atom). From thermophototropic studies of these substances, those which show the most promise for use in the space environment are $HgI_2 \cdot 2HgS$ and $HgBr_2 \cdot 2HgS$ (Table A1). $HgI_2 \cdot 2HgS$ has a decomposition temperature which is nearly twice its bleaching temperature (the most favorable ratio of the group in Table A1). $HgBr_2 \cdot 2HgS$ does not have as favorable a decomposition to bleaching temperature ratio, but does possess a relative darkening rate nearly 3 times that of $HgI_2 \cdot 2HgS$. Mercuric compounds do not bleach completely at room temperature in the absence of light; for $HgI_2 \cdot 2HgS$, the bleaching process requires 20 minutes at 90-100 °C.

Takei has taken photomicrographs of bleached $HgI_2 \cdot 2HgS$ that, according to his analysis, have shown colloidal mercury deposited on the surface. He attributes this to thermal decomposition. However, he did not report the evolution of sulfur dioxide. It should be pointed out that HgI_2 sublimes at the bleaching temperature of $HgI_2 \cdot 2HgS$. Takei's HgS was prepared by the hydrogen sulfide process, which coprecipitates Hg along with HgS; this could explain the appearance of surface deposits of colloidal mercury. The addition of 0.65-1.1 percent selenium to $HgI_2 \cdot 2HgS$ accelerated the bleaching process.

Table A1

Some Properties of $HgX_2 \cdot 2HgS$ and $HgXCNS \cdot 2HgS$ Thermal Phototropes.

Compound	Relative Darkening Rate	Decomposition Temperature (°C)	Bleaching Temperature (°C)	Color Change
$HgI_2 \cdot 2HgS$	1.0	185	90	Orange-yellow to black
$HgBr_2 \cdot 2HgS$	2.95	250	197	Pale yellow to black
$HgCl_2 \cdot 2HgS$	0.79	260	225	White to black
$HgICNS \cdot 2HgS$	0.56	213	136	Orange-yellow to black
$HgBrCNS \cdot 2HgS$	1.08	288	202	White-yellow to black
$HgICNS \cdot 2HgS$	0.026	290	260	White-yellow to black

Magnetic susceptibility studies on the compounds listed in Table A1 show: (1) Each mixture changed from a diamagnetic to a paramagnetic state at the temperature of compound formation. (2) The $HgX_2 \cdot 2HgS$ compounds were stable enough to undergo repeated thermal phototropic cycles (a contradiction to Takei's oxidation hypothesis).

The thermophototropic behavior of mercury compounds is not understood. Takei reports that a phase change takes place, but that it is entered into by less than 20 mole percent of the molecules. If, for instance, sulfur has a preference for the surface layer in the presence of illumination (at room temperature), this could explain darkening; i.e., the surface concentration of sulfur would increase (HgS can exist in a black modification). On the other hand, if iodine has preference for the surface layer at elevated temperatures, the bleaching process is explained (HgI_2 can exist in a yellow modification). This also explains the tendency of HgI_2 to distill from the surface at the bleaching temperature of $HgI_2 \cdot 2HgS$. Comsequently, the mechanism in $HgI_2 \cdot 2HgS$ appears to be a combination of molecular rotation (a phase change) and thermal diffusion.

Extensive investigations on thermal phototropic oxides have been carried out by McTaggart and Bear on titanium dioxide substrates (References A5 and A6). They investigated both anatase and rutile structures and found that only rutile gave combined thermal and optical activities. Some of their results are given in Table A2; it can be observed that no member of the table is sufficiently thermophototropic to be of use in the space environment. Table A3 gives additional results of the investigations of McTaggart and Bear from a more recent paper (Reference A6). Their conclusions are:

1. Individual crystal adsorption of the doping agent is responsible for thermal phototropism in rutile.

2. Light quanta eliminate oxygen from the rutile structure. This produces a reduced impurity and results in a fatigue effect.

3. Removal of illumination allows the oxidized impurity to return to its normal state of oxidation.

4. Heat accelerates the reduction of the oxidized impurity.

5. The presence of water vapor is necessary to free the oxygen from the rutile and make it thermophototropic.

McTaggart and Bear emphasized the importance of fusion time in the formation of phototropic oxides. It was shown, for instance, that prolonged heating at 800°C yielded no phototropic oxides. This

Table A2

Color Effects of Certain Metals in Rutile.

Element	Temp. (°C)	Fusion Time (hr.)	Unexposed Color	Exposed Color
Nd	830	1	White	Very pale pink-gray
	1020	$\frac{1}{2}$	White	Grayer
Pr	830	1	White	Very pale pink-gray
	1020	$\frac{1}{2}$	White	Grayer
Sm	830	1	White	Very pale pink-gray
	1020	$\frac{1}{2}$	White	Grayer
Co	840	1	Very pale yellow-green	Faint pink-gray
	1000	$\frac{1}{2}$	Very pale yellow-green	Pale lemon yellow
Mn	810	1	White	Pale pink-gray

Compilation of Thermophototropes.

Host	Fe	Cr	Cu	Ni	V	Mn	Bleaching of Dye*
TiO_2 (anatase)	x	+	+	+	+	+	Very fast
TiO_2 (rutile)	x	x	x	+	x	x	Very fast
Nb_2O_5	Pale cream to dark gray x	x	Off white to light brown x	+	x	x	Slow
Al_2O_3	+	x	+	+	x	+	Fast
ZnO (carbonate)	+	+	x	+	x	+	
ZnO (nitrate)	+	+	x	+	x	–	
HfO_2	+	x	–	–	–	–	
ThO_2	+	+	+	+	x	+	Slow
SnO_2	+	+	Light gray to brown x	–	–	+	Fairly fast
Ta_2O_5	+	+	Brown to tan x	–	–	+	Fast
ZrO_2	+	+	x	x	+	+	Very Slow
BeO	+	+	+	+	x	+	Slow
GeO_2	+	+	+	+	+	+	Very slow
SiO_2	+	+	+	+	+	+	Very slow
MgO	+	+	+	+	+	+	Very slow

*These compounds were mixed with chlorazol sky blue FF dye in order that bleaching rates could be checked more accurately.
xPresent.
+No observed effect.

was observed because the impurity had time to diffuse into the rutile structure from its adsorbed state on a rutile crystal.

The maximum color change occurred in rutile doped with chromic oxide—from yellow to black. However, chromium-doped rutile would not darken in the absence of oxygen, and its phototropism was destroyed when it was heated in a vacuum. When it was heated in the presence of oxygen it followed the usual behavior.

MacNevin and Ogle, Tanaka, and Weyl and Förland have studied phototropism in titanates (References A7-A9). They found that calcium titanate doped with iron, zinc, antimony, or vanadium was phototropic; the corresponding doped barium titanate was less phototropic. Silver, copper, tin, and zirconium doping agents gave no effect with either calcium or barium titanate. In contrast to the

properties of rutile phototropes, MacNevin and Ogle found that there was no fatigue effect, no oxygen effect, no water vapor effect, and no combined oxygen and water vapor effect on doped calcium and barium titanates. Their conclusions were:
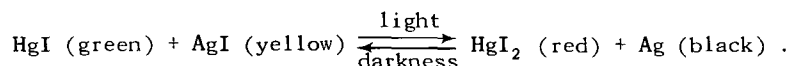
1. The metallic ion in the impurity must have a slightly different ionic radius than Ti^{+4} in order to deform the potential field and produce phototropism.

2. The charge of the metallic ion in the impurity must not be +4.

Chalkley wrote an extensive review of phototropism, in which he discussed organic (solid and liquid) and inorganic compounds (Reference A10). (In this review liquid phototropes will not be presented.) Chalkley found solid organic phototropes among the following classes of compounds: hydrazones, osazones, fulgides, stilbenes, substituted biphenyl disulfides, and substituted biphenyl disulfoxides. Unfortunately he presented no information on the absorption shifts expected from these compounds. Fatigue effects were present in organic phototropes, but without significant chemical change; whereas for inorganic phototropes fatigue effects were accompanied by drastic chemical changes. It is open to speculation, therefore, whether or not antifatigue compounds could be incorporated into certain organic phototropes. Salicylidene aniline is a notable exception; i.e., it is phototropically stable.

Chalkley briefly discussed a few inorganic phototropes—lithium amide, zinc oxide with zinc sulfide, and mercurous iodide with silver iodide. Lithium amide, which derives its phototropism from the reaction,

$$2Li_2NH \underset{\text{darkness}}{\overset{\text{light}}{\rightleftharpoons}} Li_2N + LiNH_2 \ ,$$
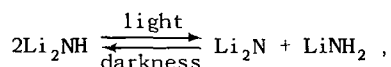
was not discussed with regard to color change or phototropic stability. Mixtures containing zinc oxide and zinc sulfide change from white to black in the presence of sunlight and moisture; the reverse reaction requires oxygen. The phototropic reaction of the mixture of mercurous iodide with silver iodide was written:

$$HgI \text{ (green)} + AgI \text{ (yellow)} \underset{\text{darkness}}{\overset{\text{light}}{\rightleftharpoons}} HgI_2 \text{ (red)} + Ag \text{ (black)} \ .$$

Unfortunately, information on possible fatigue effects and absorption shifts was not presented.

Phototropes were reported to have produced more thermoelectric power and exhibited the photoelectric effect to a greater extent than compounds of similar constitution which were not phototropic.

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